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[Contribution from the Department of Chemistry, University of Pennsylvania]

The Electric Moments of Organic Peroxides. I. Dialkyl Peroxides, Alkyl Hydroperoxides and Diacyl Peroxides[1]

By Walter Lobunez, James R. Rittenhouse and John G. Miller

The electric moments of a group of dialkyl peroxides, alkyl hydroperoxides and diacyl peroxides have been measured in benzene at temperatures in the range 20–50°. The observed moments agree with those calculated for fixed skew configurations about the peroxy grouping as in the Penney–Sutherland structure for hydrogen peroxide. In the diacyl peroxides, both of the carbonyl groups appear to face inward.

At present the most widely accepted model for the configuration of hydrogen peroxide is that proposed by Penney and Sutherland.[2] Practically all of the infrared and Raman spectral data have been correlated with this fixed skew structure[3] and the dipole moment[4] of this substance as well as the X-ray investigations of the crystalline[5a] and liquid[5b] material support this model.

Recently, Rogers and Campbell[6] have shown that di-*t*-butyl peroxide and *t*-butyl hydroperoxide have dipole moments in accord with hydrogen peroxide-like structures and that the bulk of the *t*-butyl groups appears to exert a steric effect upon the magnitude of the dihedral angle between the C–O–O planes in the dialkyl peroxide. Shortly be-

fore the publication of this work by Rogers and Campbell, an investigation of the dipole moments of some of the principal classes of organic peroxides was started here. This article reports the results for some dialkyl peroxides, alkyl hydroperoxides and diacyl peroxides.

Experimental

Preparation of Materials. Benzene.—Thiophene-free benzene was stored above sodium and refluxed over sodium shortly before use. It was then distilled with discard of the first portions of the distillate.

Di-*t*-butyl Peroxide.—A gift sample from the Shell Chemical Corporation was distilled at 98.5 mm. The fraction boiling at 52.5° was used. This was the major part of the distillate and had the refractive index n^{30}D 1.3841.

n-Butyl *t*-Butyl Peroxide.—This compound was synthesized by the method of Rust, Seubold and Vaughan.[7] It was fractionated *in vacuo*. The middle fraction, b.p. 53° (30 mm.), was used in the measurements.

t-Butyl Hydroperoxide.—Material from the Lucidol Division of the Novadel-Agene Corporation was fractionally distilled. The large fraction, comprising most of the material, b.p. 51.8° (40 mm.), n^{30}D 1.3958, was used for the measurements. A lower boiling fraction, b.p. 47–49.5° (52 mm.), was taken for separate measurement to duplicate the material (b.p. 45° at 40 mm.) used by Rogers and Campbell.[6]

Cumene Hydroperoxide.—A sample of 98% pure cumene hydroperoxide in petroleum ether was donated by the Hercules Powder Company through the courtesy of Dr. John

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(2) W. G. Penney and G. B. B. M. Sutherland, *Trans. Faraday Soc.*, **30**, 898 (1934); *J. Chem. Phys.*, **2**, 492 (1934).

(3) O. Bain and P. A. Giguere, *Can. J. Chem.*, **33**, 527 (1955).

(4) E. P. Linton and O. Maass, *Can. J. Research*, **7**, 81 (1932).

(5) (a) S. C. Abrahams, R. L. Collin and W. N. Lipscomb, *Acta Cryst.*, **4**, 15 (1951); (b) J. T. Randall, *Proc. Roy. Soc. (London)*, **159**, 82 (1937).

(6) M. T. Rogers and T. W. Campbell, This Journal, **74**, 4742 (1952).

(7) F. F. Rust, F. H. Seubold and W. E. Vaughan, *ibid.*, **72**, 338 (1950).

TABLE I

THE DILUTE SOLUTION VALUES OF THE DIELECTRIC POLARIZATION, MOLAR REFRACTION AND DIPOLE MOMENT OF THE ORGANIC PEROXIDES IN BENZENE

Compound	Temp., °C.	ϵ_{10}	α	V_{10}	β	n^2_{10}	γ	P_{20}	MRD Obsd.	MRD Theor.	μ
Di-t-butyl peroxide	30	2.2629	0.305	1.1530	0.056	2.2353	−0.303	60.86	43.0	43.52	0.94
	50	2.2231	.202	1.1818	.107	....	......	60.05	43.0		0.95
n-Butyl t-butyl per-oxide	30	2.2631	.6443	1.1518	.0731	....	......	70.95	....	42.98	1.19
t-Butyl hydroperoxide b.p. 51.8° (40 mm.)	30	2.2622	3.460	1.1516	.0483	2.2349	−0.373	91.1	24.4	24.39	1.82
	50	2.2220	2.984	1.1807	.0326	....	......	85.1	24.4		1.79
	50	2.2193	3.060	....	......	....	......	86.5	24.4		1.81
t-Butyl hydroperoxide b.p. 47–49.5° (52 mm.)	30	2.2630	3.604	....	......	....	......	93.7	....	24.39	1.86
Cumene hydroperoxide	30	2.2630	2.172	1.1530	− .194	2.2327	.0492	106.1	43.95	43.88	1.76
	30	2.2625	2.302	1.1530	− .192	....	......	109.9	43.95		1.81
Dibenzoyl peroxide	30	2.2629	1.2232	1.1525	− .331	2.2341	.126	115.4	63.84	64.05	1.60
Bis-p-chlorobenzoyl peroxide	20	2.2822	0.8046	1.1387	− .412	....	......	114.4	75.96	72.93	1.36
	30	2.2633	.7263	1.1528	− .421	2.2333	.211	111.6	75.96		1.33
Dilauroyl peroxide	20	2.2823	.2653	1.1389	− .0290	2.2516	− .188	152.2	116.1	116.89	1.32
	20	2.2825	.2721	1.1390	− .0403	....	......	151.4	116.1		1.30

H. Elliott. It was purified by conversion to the sodium salt which was washed four times with benzene and then returned to the hydroperoxide by reaction with carbon dioxide in water solution at 10°. The hydroperoxide was then extracted with benzene, the extracts being washed with water to remove inorganic salts. After removal of the benzene, the recovered hydroperoxide was analyzed by the method of Seubold and Vaughan[8] and showed a purity of 100.6%.

Dibenzoyl Peroxide.—Material of 99.5% purity was obtained from the Lucidol Division of the Novadel–Agene Corporation. It was recrystallized from chloroform by addition of methyl alcohol and was dried in a vacuum desiccator over Drierite for several days before use.

Bis-p-chlorobenzoyl Peroxide.—A gift sample was obtained from the Lucidol Division of the Novadel–Agene Corporation. After purification by the procedure of Blomquist and Buselly,[9] it was found to be 99.7% pure by the analytical method of Swain, Stockmayer and Clarke.[10]

Dilauroyl Peroxide.—Received as a gift of the Novadel–Agene Corporation, this material was purified by crystallization from n-hexane. The purified material was analyzed by iodide–thiosulfate titration and was 99.7% pure.

Apparatus and Methods.—The apparatus and procedures for measuring the dielectric constant, density and refractive index of solutions were those which have been developed and improved in this Laboratory over a long period of time.[11] Great care was exercised in excluding moisture from the solutions.

The Halverstadt and Kumler method[12] was used to calculate the infinite dilution values of both the molar polarization, P_{20}, and the molar refraction, MR_D, of the solute. These quantities, together with the electric dipole moments, μ (in debyes), evaluated from them, and the least-squares values of the intercept and associated slope terms, ϵ_{10}, V_{10}, $n^2_{10}D$, α, β and γ, for the Halverstadt and Kumler calculations are listed in Table I. The solute weight fractions, w_2, were in the range 0.00089 to 0.016. The dielectric constant of the stock benzene was measured before and after the preparation of the solutions and these two values were given equal weight with the other ϵ values in the least-squares determination of ϵ_{10} and α for each run. Table I also shows the values of the theoretical molar refractions calculated from standard bond and atomic refractions, the

(8) F. H. Seubold and W. E. Vaughan, THIS JOURNAL, **75**, 3791 (1953).

(9) A. T. Blomquist and A. J. Buselly, ibid., **73**, 3883 (1951).

(10) C. G. Swain, W. H. Stockmayer and J. T. Clarke, ibid., **72**, 5426 (1950).

(11) J. G. Miller, ibid., **56**, 2360 (1934); **60**, 42 (1938); **64**, 117 (1942); J. G. Miller and H. S. Angel, ibid., **68**, 2358 (1946); P. A. Geary and J. G. Miller, J. Electrochem. Soc., **97**, 54 (1950).

(12) I. F. Halverstadt and W. D. Kumler, THIS JOURNAL, **64**, 2988 (1942).

value for peroxidic oxygen[13] being taken as 2.19 cc. mole⁻¹. Only in the case of n-butyl t-butyl peroxide was the theoretical value of MR_D used to evaluate the moment.

The Hoecker plot[14] of w_2P_2 against w_2 gave in each case a good straight line passing through the origin, indicating that no association of the peroxides existed in the range of concentrations used.

The dipole moment of bis-p-chlorobenzoyl peroxide was measured also at 50°, but the behavior of the solutions indicated decomposition, and the moment value was low (1.10 D.), as would be expected for decomposition into CO_2, di-p-chlorophenyl and p-chlorobenzoic acid.[15]

Discussion

The moments found for di-t-butyl peroxide, 0.94 D. at 30° and 0.95 D. at 50°, are in good agreement with the value reported by Rogers and Campbell,[6] 0.92 D. at 25°, and show little effect of increase in temperature. Taking the bond moments, H–C = 0.4, C–O = 0.62, and ∠ C–O–O = 105°, as explained by Rogers and Campbell, the moment 0.94 D. corresponds to the value ϕ = 123° for the dihedral angle between the C–O–O planes in the Penney and Sutherland structure. This dihedral angle is reasonably greater than the 100° value found for hydrogen peroxide, in view of the bulk of the t-butyl groups. Molecular models show that ϕ should be of the magnitude found here.

Certainly, complete rotation of the groups about the O–O axis is impossible in the dialkyl peroxides, due to the size of the alkyl groups. The dipole moment calculated for free rotation about this axis is 1.39 D., which indicates the restriction of rotation actually present. In addition to the near constancy of the moment with change in temperature, further indication of the rigidity of the molecule comes from calculation of the moment expected for free oscillation outside the region (2ϕ = 246°) excluded by the barrier to cis configuration. This calculated value is 0.6 D., showing that the barrier to trans configuration is also appreciable.

In going to n-butyl t-butyl peroxide, the moment rises to 1.19 D. corresponding to a dihedral angle of

(13) N. Milas, D. M. Surgenor and L. H. Perry, ibid., **68**, 1617 (1946).

(14) F. E. Hoecker, J. Chem. Phys., **4**, 431 (1936).

(15) A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954, p. 85.

105°, as expected from replacement of one of the *t*-butyl groups by a *n*-butyl group. Similarly, Rogers and Campbell[6] found that the electric moment of di-*n*-butyl disulfide is greater than that of di-*t*-butyl disulfide by an amount indicating a dihedral angle smaller by about 10°. Earlier work in this Laboratory[16] showed that the dipole moments of polysulfides in general give proof of the existence of rigid skew structures for the polysulfide groupings, which are expected to use bonding orbitals similar to those in the peroxides.

Turning to the alkyl hydroperoxides, the value found here for *t*-butyl hydroperoxide is slightly different from that, 1.87 D., reported by Rogers and Campbell,[6] who measured material of boiling point 45° at 40 mm. We have found that the main fraction in the distillation of *t*-butyl hydroperoxide boils at 51.8° under their pressure, 40 mm. This material has a constant moment averaging 1.81 D. over the range 30–50°, a value much closer to the value, 1.78 D., calculated[6] for a rigid skew structure with $\phi = 100°$. The lower-boiling fraction (47–49.5° at 52 mm.) obtained in the fractionation of the *t*-butyl hydroperoxide has a moment of 1.86 D., indistinguishable from the value obtained by Rogers and Campbell, and apparently contains a polar impurity.

When one changes from *t*-butyl to cumene hydroperoxide by replacing one of the methyl groups of the former by a phenyl group, no discernible change in moment takes place. This near equality of moments is the same as observed hitherto for other benzyl and benzal compounds in comparison with the corresponding alkyl compounds.[17] In the present case, this equality is to be expected from the probability that any electronic charge drawn away from the phenyl ring by the peroxy group would be largely compensated by the usual charge shifts in the opposite direction due to interaction of the phenyl group with the alkyl groups. The moment observed for cumene hydroperoxide may therefore be considered good confirmation of the findings obtained for *t*-butyl hydroperoxide, namely, that the alkyl hydroperoxides, like the dialkyl peroxides, show moments in accord with hydrogen peroxide-like structures.

Interpretation of the electric moment values of the diacyl peroxides would appear to be complicated by additional modes of intramolecular rotation and the effects of resonance due to the carbonyl and phenyl groups present. The rotations pictured in the following reference diagram show the dihedral angles to be considered
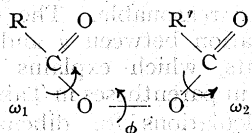

These rotations are all that need be considered for the three peroxides under consideration in view

of the strong evidence that the C–C–O atoms in carboxylate groups are in fixed coplanar arrangement.

Although severe restriction of rotation about the O–O axis would be expected from the bulk of the acyl groups as well as the mutual repulsion of the pπ electrons on the peroxy oxygen atoms, the effects of resonance must also be considered. Since structures such as
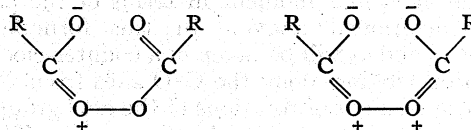
are probably involved, it would appear that the ω values would be fixed at 0 or 180° due to the coplanarity requirements. At the same time, it would be difficult to predict the net effect of interaction of such structures with the peroxy grouping. It is possible that the Penney–Sutherland barrier to rotation about the O–O axis might be lowered since the resonance appears to utilize the pπ-electrons of the peroxy oxygen atoms in double bond formation with the two carbonyl carbon atoms. On the other hand, the charges placed on the carbonyl oxygen atoms would raise the barrier to rotation about the O–O axis. In all three of the diacyl peroxides the adjacent charges placed on the peroxy group would also be expected to lower the stability of the forms pictured above and hence to minimize that resonance. In dibenzoyl peroxide and bis-*p*-chlorobenzoyl peroxide, additional resonance forms such as
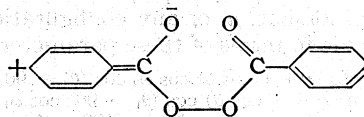
would be expected to diminish the double bond character of the links connecting carbon to peroxy oxygen, due to competition with the other resonance forms.

In view of these complications it will be helpful to compare the observed moments with those calculated for different internal rotations. In these calculations, the effect of other parameters, namely, the bond moments and bond angles, must be considered also. With regard to the latter, the bond angles of the carbonyl carbon and the peroxy oxygen atoms would be expected to vary only slightly from the values $\angle$ C–C–O = 110°, $\angle$ O=C–O = 125°, $\angle$ C–O–O = 105°, and we shall fix them at those values for all of the calculations. For the bond moments C–O, C=O, it has been found[18] that resonance in the phenyl ring makes very little contribution to the moments of the phenyl ketones and aromatic carboxylic acids such as benzoic acid and *p*-chlorobenzoic acid, so that we should expect no large effect upon those bond moments in changing the acyl group from lauroyl to benzoyl or *p*-

(16) C. C. Woodrow, M. Carmack and J. G. Miller, *J. Chem. Phys.*, **19**, 951 (1951).

(17) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p. 317.

(18) M. E. Hobbs and A. J. Weith, Jr., This Journal, **65**, 967 (1943); C. S. Brooks and M. E. Hobbs, *ibid.*, **62**, 2851(1940); C. P. Smyth, ref. 17, pp. 253, 308, 319.

chlorobenzoyl. In the acyl peroxides studied here, the only other moment to consider is that due to the alkyl or aryl group attached to the carbonyl carbon atom. In each case this moment will be directed along the axis of attachment to the carbonyl carbon atom and this resultant R–C moment will vary with the nature of the R group.

For the purpose of correlating the observed moments with those calculated for different assignments for the dihedral angles and group or bond moments, we have developed a general expression for the molecular moment in terms of the parameters mentioned above. In this formula, the angles ω_1 and ω_2 will be taken in a counter-clockwise direction looking along the C–O axes from C to O for measurement of rotations of the acyl groups out of the plane containing the O–O axis. The coplanar arrangement shown in the reference diagram specifies the zero values of ω_1 and ω_2. The angle ϕ will be measured in a counter-clockwise direction looking along the O–O axis from right to left for measurement of rotations of the right-hand C–O–O plane out of the coplanar arrangement with the other C–O–O plane.

The R–C, C=O and C–O moments of the carboxylate group on the left will be symbolized a, b and c, respectively, and the corresponding moments for the other group will be written, e, d and f. When these moments are oriented in the customary manner, e.g., R → C, C → O, the moments are positive in sign. The bond angles for the left-hand and right-hand C–O–O groupings will be symbolized θ_1 and θ_2, respectively. Finally, we will take $\angle$ C–C–O = $90°$ + α, and $\angle$ O=C–O = $90°$ + β for the acyl group on the left with γ and δ the corresponding values for the group on the right. The following expression then gives the molecular moment, μ, of any configuration of a diacyl peroxide in terms of these parameters.

$$\mu^2 = [(e\cos\gamma + d\cos\delta)\cos\omega_2\cos(\theta_2 - 90) \\ + (a\cos\alpha + b\cos\beta)\cos(\theta_1 - 90)\cos\omega_1 \\ - (f + e\sin\gamma - d\sin\delta)\cos(180 - \theta_2) \\ + (c + a\sin\alpha - b\sin\beta)\cos(180 - \theta_1)]^2 \\ + [-(f + e\sin\gamma - d\sin\delta)\sin(180 - \theta_2)\sin\phi \\ - (e\cos\gamma + d\cos\delta)\sin\omega_2\cos\phi \\ - (e\cos\gamma + d\cos\delta)\sin(\theta_2 - 90)\cos\omega_2\sin\phi \\ - (a\cos\alpha + b\cos\beta)\sin\omega_1]^2 \\ + [-(f + e\sin\gamma - d\sin\delta)\sin(180 - \theta_2)\cos\phi \\ + (e\cos\gamma + d\cos\delta)\sin\omega_2\sin\phi \\ - (e\cos\gamma + d\cos\delta)\sin(\theta_2 - 90)\cos\omega_2\cos\phi \\ - (c + a\sin\alpha - b\sin\beta)\sin(180 - \theta_1) \\ + (a\cos\alpha + b\cos\beta)\sin(\theta_1 - 90)\cos\omega_1]^2$$

For a symmetric diacyl peroxide, the formula simplifies greatly because of the equalities $a = e$, $b = d$, $c = f$, $\alpha = \gamma$, $\beta = \delta$, $\theta_1 = \theta_2 = \theta$. Furthermore, we shall fix the bond angles, as mentioned above, at the values $\alpha = 20°$, $\beta = 35°$, $\theta = 105°$. Table II shows some of the calculations made with the use of the formula with respect to lauroyl peroxide. The first ten rows of that table show the effects of the dihedral angles and the last three rows consider the effects of the bond or group moments.

In considering the dihedral angle, the R–C and C–O moments are fixed at the values used for the alkyl peroxides and hydroperoxides and the C=O moment is assigned the normal value,[19] 2.3 D., on the basis mentioned above, that these moments are

(19) C. P. Smyth, ref. 17, p. 245.

TABLE II

THE EFFECTS OF DIHEDRAL ANGLES AND BOND MOMENTS ON THE MOLECULAR MOMENT OF DILAUROYL PEROXIDE

ϕ	ω_1	ω_2	a	b	c	μ
Free rot.	Free rot.	Free rot.	0.4	2.3	0.62	3.30
100	Free rot.	Free rot.	.4	2.3	.62	3.27
Free rot.	0	180	.4	2.3	.62	1.60
Free rot.	0	0	.4	2.3	.62	4.51
Free rot.	180	180	.4	2.3	.62	4.51
100	0	180	.4	2.3	.62	1.45
109	0	180	.4	2.3	.62	1.31
180	0	180	Any	Any	Any	0
100	180	0	0.4	2.3	0.62	0.05
100	0	0	0.4	2.3	.62	4.52
100	0	180	1.65 (25.0)	2.3	.62	1.31
100	0	180	0.4	2.16 (−0.50)	.62	1.31
100	0	180	0.4	2.3	0.73 (2.84)	1.31

little affected by the resonance pictured for the molecule. The three calculations in which free rotation is taken only about the O–O axis give in each case the same moment value as if ϕ were fixed at 90°. With this and the coplanarity requirements for the carboxylate groups as well as the bulk of those groups in mind, all of the calculations of the effects of the rotations indicate strongly that only a fixed structure with the approximate values $\omega_1 = 0°$, $\omega_2 = 180°$ fits the observed value, 1.31 D. In fact, with ϕ = 100° and taking the sixteen possible combinations of 0°, 90°, 180°, 270° values for ω_1 and ω_2, this is the only combination which gives a moment within 1.1 D. units of the observed value. As to ϕ, a value slightly larger than the Penney–Sutherland 100° value is approximated, but it would be superfluous to refine the interpretations beyond this point.

The last three rows of Table II show the calculations of the group and bond moments corresponding to the fixed structure of observed moment, 1.31 D. Fortunately, as might be expected from the spatial direction of the moments, the moment of the molecule is found not greatly dependent on the R group moment, a, which is apt to be the most questionable of the component moments. With b and c, small changes affect μ greatly, and the results indicate that the assignments 2.3 and 0.62 are quite reasonable. The formula gives a quadratic relation between μ and the group and bond moments, which explains the improbable values shown in parentheses in Table II.

Similar calculations for dibenzoyl and bis-p-chlorobenzoyl peroxide confirm the indication that the diacyl peroxides have fixed skew structures with the carbonyl groups facing inward. Here, with b and c the same as for dilauroyl peroxide, the usual values of the phenyl and p-chlorophenyl group moments, 0 and −1.6 D., respectively, appear satisfactory.

Oesper and Smyth[20] measured the moments of dibenzoyl peroxide and dibenzoyl persulfide. For the former, they reported the value 1.58 D. at 45° in benzene, nearly the same value as reported here for 30° in the same solvent, and for the persulfide they obtained the values 1.1 D. at 25° and 1.4 D. at 45° in benzene. Taking all the other parameters the same as we have taken them for dibenzoyl peroxide, the moments for the persulfide correspond to a C → S moment of 0.94 D. in the one case and 0.7 D. in the other. The amounts by which these moments exceed the C → O moment lie in a reasonable range for the change from oxygen to sulfur.[20]

(20) P. F. Oesper and C. P. Smyth, THIS JOURNAL, **64**, 768 (1942).

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